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**Feature Article**

**Supramolecular Polymerization from Controllable Fabrication to Living Polymerization**

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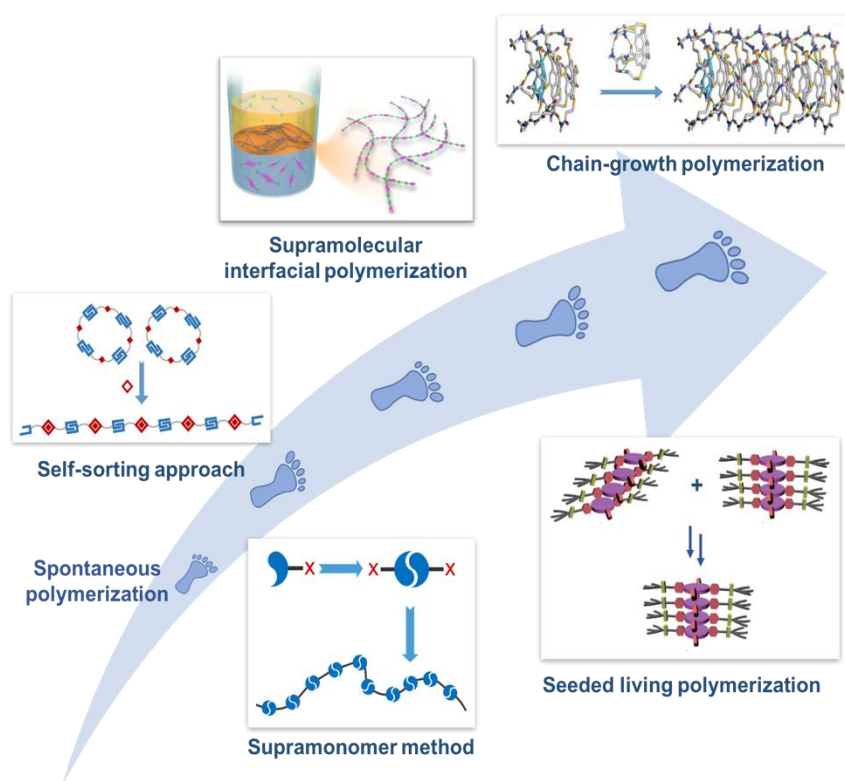
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Supramolecular polymers have attracted lots of interests in the scientific community; however, developing controllable methods of supramolecular polymerization remains a big challenge. This article reviews some recent developments of methods for supramolecular polymerization from controllable fabrication to living polymerization. Three facile methods with general applicability for controllable fabrication of supramolecular polymers have been established recently: the first method is a self-sorting approach by manipulating ring–chain equilibrium based on noncovalent control over rigidity of monomers; the second is the covalent polymerization from supramonomers formed by noncovalent interactions; and the third is supramolecular interfacial polymerization. More excitingly, living supramolecular polymerization has been achieved by two elegant strategies, including seeded supramolecular polymerization under pathway complexity control and chain-growth supramolecular polymerization by metastable monomers. It is anticipated that this review may provide some

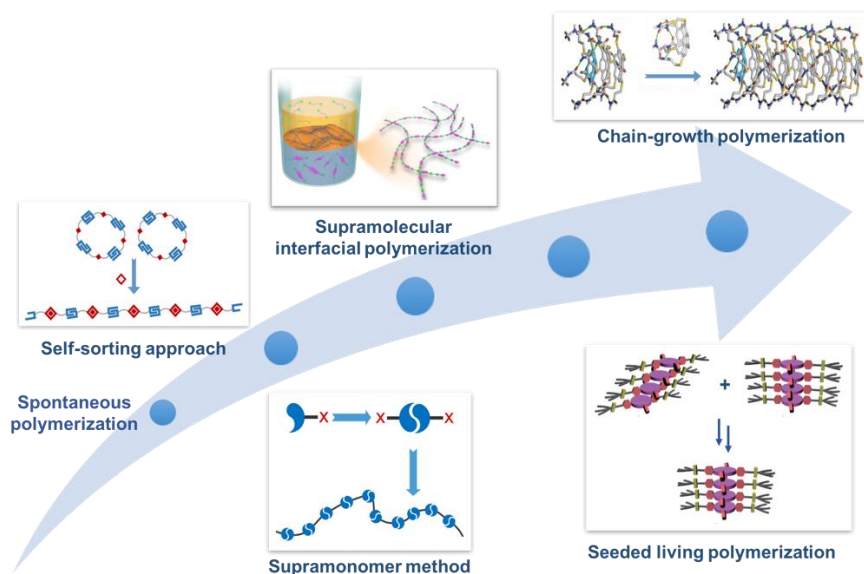
guidance for precise fabrication of supramolecular polymers, leading to the construction of supramolecular polymeric materials with controllable architectures and functions.



## 1. Introduction

Supramolecular polymers, emerging from the marriage between supramolecular chemistry and polymer science, have been widely studied for more than twenty years.<sup>[1]</sup> A supramolecular polymer is usually defined as a “polymeric array of monomeric units that are held together by highly directional and reversible noncovalent interactions”. Based on the reversibility of noncovalent interactions, supramolecular polymers are endowed with many unique characteristics including self-healing, easy processability and stimuli-responsiveness, thus attracting lots of interests from scientists in the fields of polymer science, material science, nanoscience and technology.<sup>[2-11]</sup>

Much effort has been devoted to expand the research area of supramolecular polymers. As far as supramolecular polymer chemistry is concerned, there are a number of issues that are drawing the attention of the community. The first is to exploit diversified and efficient noncovalent interactions as the driving forces for supramolecular polymerization.<sup>[12-33]</sup> The second is to demonstrate various applications of supramolecular polymers in many interdisciplinary fields based on their unique dynamic properties.<sup>[34-51]</sup> The third is to develop a variety of effective methods for supramolecular polymerization, from controllable fabrication to living polymerization.<sup>[52-56]</sup> Since there are many reviews about driving forces, characterization<sup>[57]</sup> or functionalization of supramolecular polymers, this feature article does not aim to provide comprehensive reviews in all aspects, but only focuses on some recent developments of supramolecular polymerization from controllable fabrication to living polymerization, as shown in **Figure 1**.



*Figure 1.* Schematic representation of the recent developments of methods for supramolecular polymerization from controllable fabrication to living polymerization.

By employing one or more bifunctional or multi-functional monomers, supramolecular polymers and polymeric networks can be easily and spontaneously formed through noncovalent interactions. In the early stages of the history of supramolecular polymers, most of them were prepared by spontaneous supramolecular polymerization. Owing to the dynamic nature of noncovalent interactions, thermodynamic control over spontaneous supramolecular polymerization can be achieved by regulating the concentration, solvent, temperature and addition of depolymerizing agents. For instance, Meijer and co-workers have reported that increasing the concentration of bifunctional monomers, bearing multiple hydrogen-bonding units, can decrease the possibility for intramolecular cyclization, thus driving the ring–chain equilibrium from cyclic oligomers to linear polymers.<sup>[16]</sup> Since hydrogen bonding is sensitive to temperature, the degree of polymerization of these supramolecular polymers can also be controlled and decreased at high temperature. Additional monofunctional monomers can act as a chain stopper to depolymerize the polymers. Despite these simple controls based on the thermodynamic factors, it still remains a challenge to realize controllable fabrication of supramolecular polymers through chain structural regulation.

After intensive investigations into cucurbit[n]uril-based supramolecular polymers for a number of years, we realized that the rational design of monomers to avoid the cyclization and dimerization is essential to promote linear supramolecular polymerization.<sup>[18, 20, 58-61]</sup> Based on this knowledge, we initiated investigations into thermodynamic control over supramolecular polymerization through a self-sorting approach.<sup>[53]</sup> Here we introduced a rigid noncovalent unit into the core of the bifunctional monomer for reversibly tuning the rigidity of monomers, thus realizing control over the ring-chain equilibrium involved in supramolecular polymerization. In addition, since spontaneous polymerization is hard to control, we tried to use this aspect to our advantage. We then created a so-called supramonomer method for controllable fabrication of supramolecular polymers.<sup>[62-63]</sup> This supramonomer method entails first fabricating supramonomers through noncovalent interactions and then producing supramolecular polymers by conventional covalent polymerization of the supramonomers. The challenge of manipulating spontaneous supramolecular polymerization is therefore transferred to become a tractable conventional covalent polymerization. Moreover, in the case where one monomer is water-soluble and the other is oil-soluble, we have very recently developed a new method of supramolecular interfacial polymerization. We are thus able to fabricate supramolecular polymers with controllable molecular weights and chain structures in the above three ways.

Although several methods for controllable fabrication of supramolecular polymers have been established, achieving living supramolecular polymerization remains a “Holy Grail” in this field. Along with the rise of supramolecular systems chemistry,<sup>[64]</sup> thermodynamic control over self-assembled systems is not enough anymore, but kinetic control begins to become more urgent and important. To inhibit spontaneous polymerization under kinetic control is the key to devise living supramolecular polymerization. Very inspiring, two elegant strategies have been presented and demonstrated: the first by seeded polymerization under pathway complexity control and the second by chain-growth

polymerization from metastable monomers. As for the first strategy, Sugiyasu, Takeuchi and co-workers designed a nucleation-elongation process coupled with a pre-equilibrium of kinetically trapped pre-assemblies from monomers, which can suppress spontaneous polymerization.<sup>[54]</sup> With the addition of an aliquot of thermodynamically stable seeds into the pre-assemblies, these seeds can be elongated to form linear supramolecular polymers in a living manner. As for the second strategy, Aida and Miyajima and co-workers presented a creative concept of a “metastable monomer”, which refers to a monomer that is kinetically restricted from step-growth polymerization, but able to be supra-polymerized by mixing with tailor-made initiators with characteristics of living polymerization.<sup>[55]</sup> In general, these two strategies represent two different ways for preventing the monomers from spontaneous polymerization through kinetic controls: one is through intermolecular pre-assembling, and the other through intramolecular self-restriction. These two methods have established the fundamentals of living supramolecular polymerization. We anticipate that these research efforts will inspire further investigations to diversify these concepts for achieving supramolecular polymerization in a living manner.

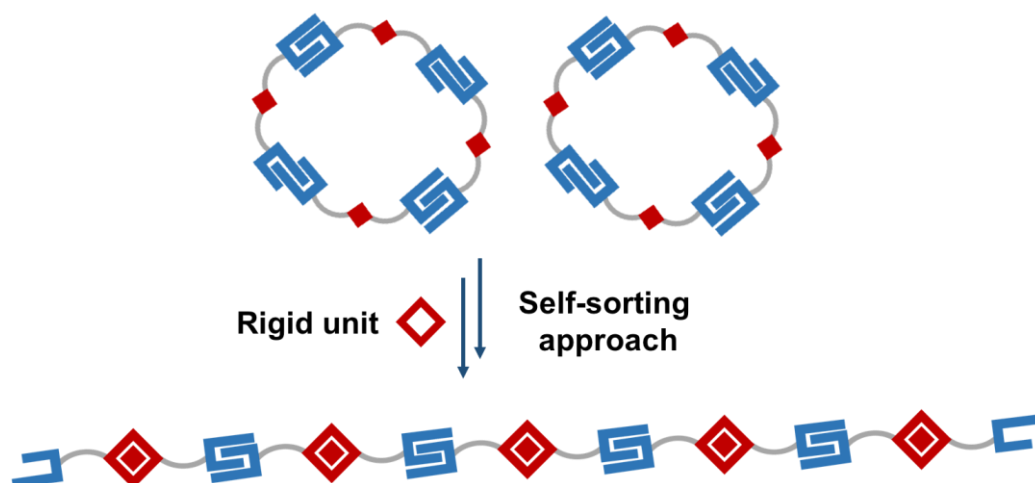
In the following review, recent progress in these areas will be described in detail. Their essential principles will be summarized, thus providing guidance to scientists in the field to promote the development and continued exploration of supramolecular polymerization.

## **2. Controllable Fabrication of Supramolecular Polymers**

### **2.1. Controllable Supramolecular Polymerization by Self-sorting**

Ring–chain equilibrium is a characteristic phenomenon during step-growth supramolecular polymerization because of the reversible nature of noncovalent interactions. Manipulating this equilibrium is the key to realize thermodynamic control over supramolecular polymerizations. To this end, our group presented a facile method of supramolecular polymerization controlled

and promoted through self-sorting. Self-sorting is a self-assembling process in which molecules are able to selectively and specifically bind with their own recognition units within a multicomponent mixture. Our self-sorting approach is to introduce a rigid recognition unit into the core of a bifunctional monomer based on one type of noncovalent interaction and then supra-polymerize these monomers by another type of noncovalent interaction. By simply tuning the ratio of rigid units in the polymer chain on the basis of their reversibility, the ring–chain equilibrium of supramolecular polymerization can be controlled as shown in **Figure 2**.

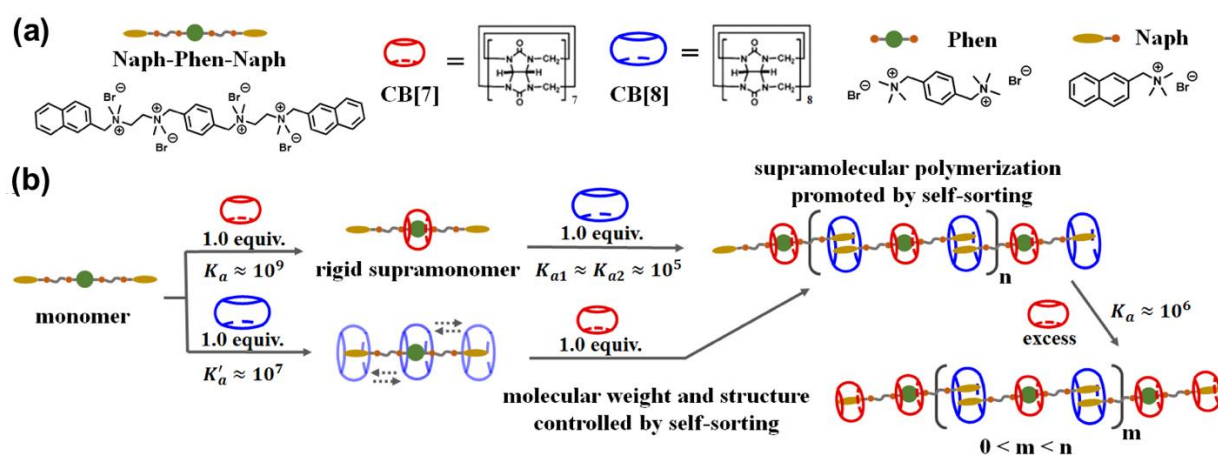


*Figure 2.* Schematic representation of controlling the ring–chain equilibrium during supramolecular polymerization through a self-sorting approach.

To demonstrate this approach, a bifunctional monomer (Naph-Phen-Naph) containing one *p*-phenylene moiety in the middle flanked by two naphthalene moieties as end groups was prepared as shown in **Figure 3a**.<sup>[53]</sup> We envisioned that the *p*-phenylene moiety in the middle of the bifunctional monomer could selectively bind with cucurbit[7]uril (CB[7]) to construct a rigid core through a self-sorting process, thus facilitating free access to the naphthalene end groups for complexation with cucurbit[8]uril (CB[8]) in a molar ratio of 2:1 and leading to the formation of linear supramolecular polymers. To confirm the above self-sorting process, we prepared two model compounds bearing the *p*-phenylene moiety (Phen) and the naphthalene



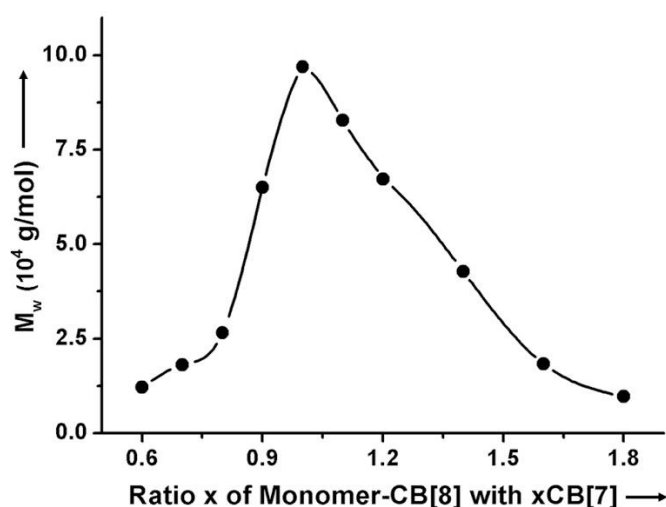
moiety (Naph), respectively. Clearly indicated by  $^1\text{H}$  NMR spectroscopy, only the host-guest complex of Phen-CB[7] and the host-guest complex of 2Naph-CB[8] were observed in the mixture of Phen, CB[7], Naph and CB[8] at the molar ratio of 1:1:2:1, thus elucidating that self-sorting indeed occurs. The mechanism behind self-sorting was investigated by extensive isothermal titration calorimetry (ITC) experiments to obtain the thermodynamic information about the host-guest chemistry during the self-sorting process. As shown in **Figure 3b**, the binding constant for Phen-CB[7] is as high as  $10^9 \text{ M}^{-1}$ , which is 180 times higher than the binding constant for Phen-CB[8]. The stepwise binding constants for each of the Naph units in the 2:1 homoternary complex with CB[8] were only around  $10^5 \text{ M}^{-1}$ . Therefore, a possible mechanism would involve CB[7] strongly binding to the *p*-phenylene moiety on account of its remarkably high binding affinity, thus allowing the CB[8] easy access to the Naph end groups. Employing this efficient self-sorting approach, supramolecular polymers can be fabricated by equimolar mixing of Naph-Phen-Naph, CB[7] and CB[8] in water.



**Figure 3.** (a) Chemical structures of the designed monomer Naph-Phen-Naph, CB[7], CB[8] and two model compounds, Phen and Naph; (b) Schematic diagram of cucurbituril-based supramolecular polymerization promoted by self-sorting upon equimolar mixing of CB[7], CB[8] and Naph-Phen-Naph, and controlled depolymerization of the supramolecular

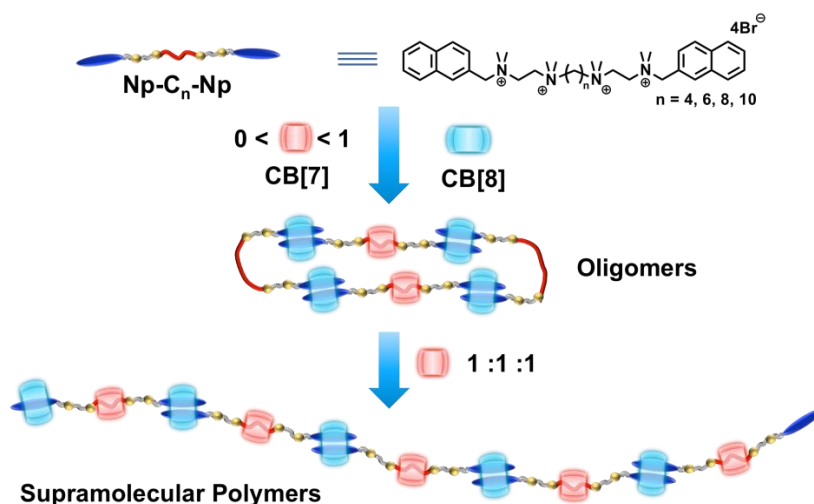
polymers in the presence of excess CB[7]. Reproduced with permission.<sup>[53]</sup> Copyright 2014, John Wiley & Sons, Inc.

One advantage of this self-sorting approach is the facile control over the molecular weight of supramolecular polymers by simply tuning the molar ratio of CB[7] to Naph-Phen-Naph-CB[8]. The molecular weight and distribution of supramolecular polymers were characterized by asymmetric flow field flow fractionation (AsF-FFF). By gradually adding CB[7] into the solution of Naph-Phen-Naph-CB[8], more and more rigid cores were formed to promote the linear supramolecular polymerization. As shown in **Figure 4**, when the molar ratio of CB[7] and Naph-Phen-Naph-CB[8] approached 1.0, supramolecular polymers with the highest molecular weight around  $9.7 \times 10^4 \text{ g mol}^{-1}$  were obtained with a polydispersity of 1.5. When the ratio of CB[7] exceeded 1.0 equivalent, an excess of CB[7] acted as a depolymerization agent to degrade the supramolecular polymers by displacing naphthalene moieties from their complexation with CB[8]. During the whole process, the degree of supramolecular polymerization can be well tuned from oligomers ( $1.0 \times 10^4 \text{ g mol}^{-1}$ ) to polymers ( $9.7 \times 10^4 \text{ g mol}^{-1}$ ).



*Figure 4.* Ratio-dependent plot of supramolecular polymer molecular weights in the CB[7]-titration experiment, as measured by AsF-FFF. Reproduced with permission.<sup>[53]</sup> Copyright 2014, John Wiley & Sons, Inc.

To demonstrate the applicability of the self-sorting approach, we further extended this strategy to the self-sorting system of aliphatic and aromatic motifs.<sup>[65]</sup> For this purpose, a bifunctional monomer (Np-C<sub>n</sub>-Np) bearing an alkyl chain (C<sub>n</sub> ; n = 4, 6, 8, 10) and two naphthalene moieties (Np) was designed and prepared as shown in **Figure 5**. By mixing the monomer with CB[7] and CB[8], the selective complexation between C<sub>n</sub> and CB[7] can construct a rigid core to avoid dimerization and cyclization, two factors that will influence supramolecular polymerizations unfavorably. As a result, the host-guest complexation between Np and CB[8] can drive the supramolecular polymerization. Adjustment of the length of the alkyl chain can influence the degree of polymerization. It turns out that the hexyl chain (n = 6) is the best choice for fabricating a high-molecular-weight supramolecular polymer. In addition, the kinetics of the linear supramolecular polymerization were further studied by stopped flow technique. The results of stopped flow investigations indicated that the formation of the rigid core can be completed within 1.0 s while the process of supramolecular polymerization takes place on a longer time scale of approximately 20.0 s.

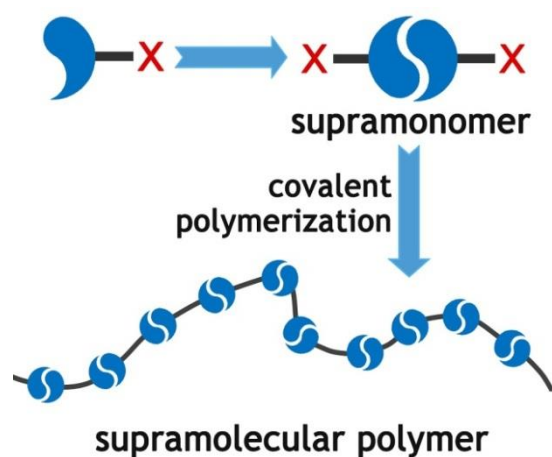


*Figure 5.* Schematic representation of supramolecular polymerization promoted and controlled through self-sorting of aliphatic and aromatic motifs. Adapted with permission.<sup>[65]</sup>  
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To successfully control the supramolecular polymerization by a self-sorting approach, the rational design of a self-sorting system is of great importance. The key point is that the two kinds of noncovalent interactions used for controlling the rigidity of monomers and driving the supramolecular polymerization should be orthogonal. Especially, the binding affinity for the noncovalent interaction to fabricate the rigid core should be high enough to avoid interference with the second type of noncovalent interaction employed. In addition, the rigid core should be bulky and rigid enough to suppress the dimerization and cyclization. It should be noted that many other self-sorting systems based on noncovalent interactions can be utilized to promote and control supramolecular polymerizations.<sup>[66-67]</sup> Additionally, this strategy can be applied to fabricate supramolecular polymers not only with linear topologies but also hyperbranched, alternating and cross-linked architectures.<sup>[68-71]</sup>

## **2.2. Fabricating Supramolecular Polymers by A Supramonomer Method**

Inspired by the concept of macromonomer in polymer science, our group devised a new concept of a “supramonomer”, which refers to a monomer that is fabricated by noncovalent interactions, but is able to polymerize using covalent methods of polymerization, as shown in **Figure 6**.<sup>[52, 63, 72-74]</sup> This supramonomer method can be considered to be a problem-transfer strategy. The difficult problem of manipulating spontaneous step-growth supramolecular polymerization is transferred to become a tractable conventional covalent polymerization. Since the conventional covalent methods for polymerization are well-studied and developed, we are able to achieve controllable fabrication of supramolecular polymers in this way.



*Figure 6.* Schematic representation of our supramonomer method by polymerizing supramonomers with conventional covalent methods. Reproduced with permission.<sup>[72]</sup> Copyright 2017, John Wiley & Sons, Inc.

As a proof of concept, a supramonomer linked by CB[8]-mediated host-guest complexation, containing two alkyne moieties as the terminal groups, was prepared.<sup>[52]</sup> As shown in **Figure 7**, the specific host-guest complex between CB[8] and two tripeptide Phe-Gly-Gly derivatives (FGGP) was chosen as the noncovalent linker. The binding affinity of this interaction was confirmed to be as high as  $3.45 \times 10^{10} \text{ M}^{-2}$  by ITC, which guaranteed the stability of the supramonomers for the click polymerization reaction to follow. A copper-catalyzed azide-alkyne click polymerization was then performed by equimolarly mixing the supramonomer and diazido-terminated poly(ethylene glycol) ( $\text{N}_3\text{-PEG-N}_3$ ) in the presence of the copper catalyst. Supramolecular polymers were prepared successfully by the click polymerization of the supramonomers.

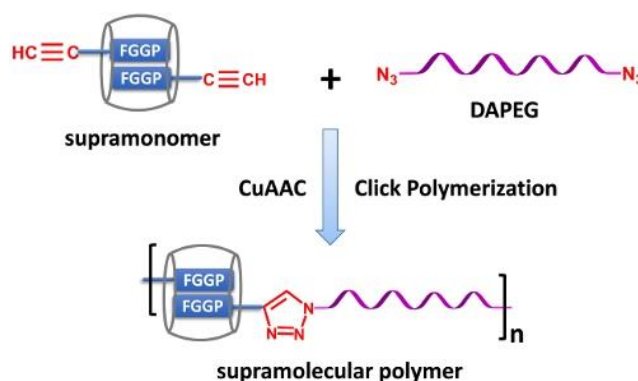
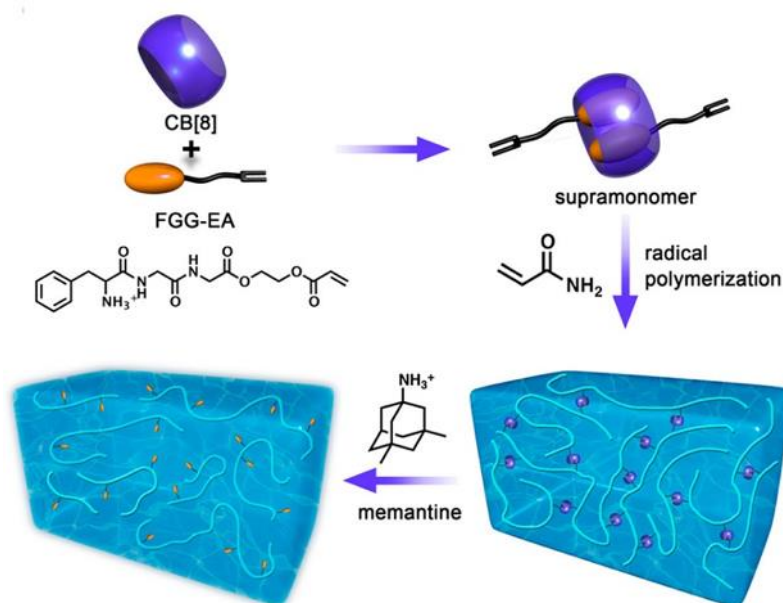


Figure 7. Schematic representation of copper-catalyzed azide-alkyne click polymerization from supramonomers formed by CB[8]-mediated homoternary complexation. Reproduced with permission.<sup>[52]</sup> Copyright 2014, The Royal Society of Chemistry.

This supramonomer method can be applied to many other covalent methods of polymerization for fabricating supramolecular polymers. It is very exciting that many further attempts at the construction of linear supramolecular polymers from supramonomer were successful through thiol-ene click polymerization, olefin metathesis polymerization, and enzyme-triggered covalent condensation.<sup>[62, 75-76]</sup> Taking the olefin metathesis polymerization as an example, supramonomers were fabricated by dimerization of styrene-terminated ureido-pyrimidinones (UPy) driven by quadruple hydrogen bonds. Then, supramolecular polymers were obtained by olefin metathesis of these supramonomers. Benefiting from the photo-responsiveness of stilbene units and the dynamic behavior of double bonds in the presence of ruthenium catalysts, the molecular weight of the supramolecular polymer was regulated through reversible conformational modulation by UV irradiation and ruthenium catalysts. The supramonomer method is therefore also applicable to many other noncovalent systems.



*Figure 8.* Schematic representation of supramolecular hydrogels fabricated by conventional monomers and supramonomers as a cross-linker, which is used as an easy-to-remove wound dressing material. Reproduced with permission.<sup>[77]</sup> Copyright 2017, American Chemical Society.

Supramonomers can also function as supramolecular cross-linkers to fabricate supramolecular cross-linked materials with dynamic properties, such as microgels and hydrogels. As shown in **Figure 8**, a supramonomer bearing two acrylate moieties was prepared by specific host-guest complexation between Phe-Gly-Gly derivatives (FGG-EA) and CB[8] in a molar ratio of 2:1. This supramonomer with two acrylate moieties as end groups was then employed as a supramolecular cross-linker to copolymerize with N-isopropylacrylamide (NIPAM) and acrylamide (AAM) to obtain supramolecular microgels and hydrogels, respectively.<sup>[77-78]</sup> It should be pointed out that the dynamic nature of host-guest complexation endows these materials with attractive properties of stimuli-responsiveness and easy degradability. 3, 5-Dimethyl-1-adamantanamine hydrochloride (DAMDA), a Food and Drug Administration (FDA) approved drug, is a strong competitive guest and capable of replacing FGG from the host-guest complex of 2FGG-CB[8]. Thus, it

was chosen as a chemical stimulus to quantitatively disassociate the supramonomers, thus degrading these supramolecular microgels and hydrogels. More excitingly, the supramolecular hydrogel cross-linked by supramonomers becomes an easy-to-remove wound dressing material, which can avoid additional trauma to newly formed tissue during repeated wound dressing changes.

For successful fabrication of supramolecular polymers from supramonomers, three essential points should be considered simultaneously. First, the noncovalent linkage of supramonomer should be constructed by interactions with high affinity. Second, the covalent polymerization should be performed with high efficiency. Third, the above two events should be orthogonal and proceed without any interference. It should be mentioned that this strategy is of general applicability and not only limited to fabricating linear supramolecular polymers, but can also be utilized in construction of branch-like, star-shaped or cross-linked supramolecular polymers. It is highly anticipated that this strategy could be extended to fabricate functional supramolecular materials for drug delivery, chemical separation, 3D-printing and so forth.

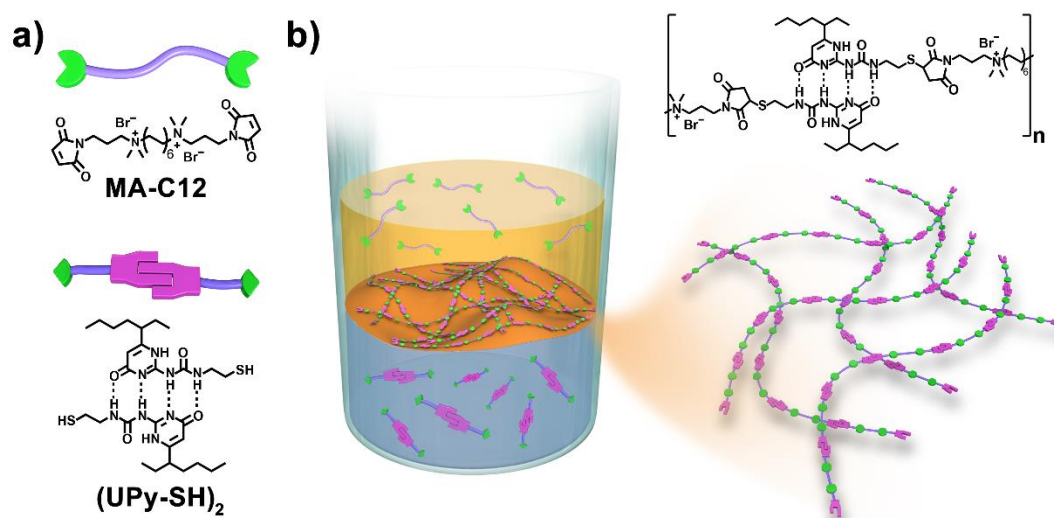
## **2.2. Supramolecular interfacial polymerization**

Supramolecular polymers are normally fabricated in homogenous media, which means the monomers should be dissolved in the same solvent. However, when one monomer is water-soluble and the other is oil-soluble, traditional homogenous supramolecular polymerization can be ruled out. Thus, there exists urgent and wide-spread demand to develop supramolecular interfacial polymerizations to address this challenge. Considering that the molar ratio of the monomers must be strictly controlled for preparing supramolecular polymers with high molecular weight in homogenous media, one of the advantages of supramolecular interfacial polymerization is that it can be insensitive to the molar ratio of



monomers. Therefore, supramolecular interfacial polymerization can provide a facile method for constructing supramolecular polymers with controlled compositions and structures.

Inspired by traditional interfacial polymerization, two different monomers were designed and prepared to be dissolved in two immiscible solvents. As shown in **Figure 9a**, one of the monomers is an oil-soluble supramonomer ((UPy-SH)<sub>2</sub>) which contains two thiol end groups linked by two ureidopyrimidinone units; and the other is a water-soluble monomer (MA-C12) bearing two maleimide end groups.<sup>[79]</sup> With the addition of an aqueous solution of MA-C12 onto the surface of a solution of the supramonomer (UPy-SH)<sub>2</sub> in CHCl<sub>3</sub>, supramolecular polymeric films were formed at the water-oil interface within one minute (**Figure 9b**). Additionally, the glass transition temperature of supramolecular polymers could be well tuned via simply regulating the polymerization time and temperature.



*Figure 9.* (a) Chemical structures of the oil-soluble supramonomer (UPy-SH)<sub>2</sub> and the water-soluble monomer (MA-C12); (b) A schematic representation of supramolecular interfacial polymerization at the water-oil interface.<sup>[79]</sup> Copyright 2017 John Wiley & Sons, Inc.

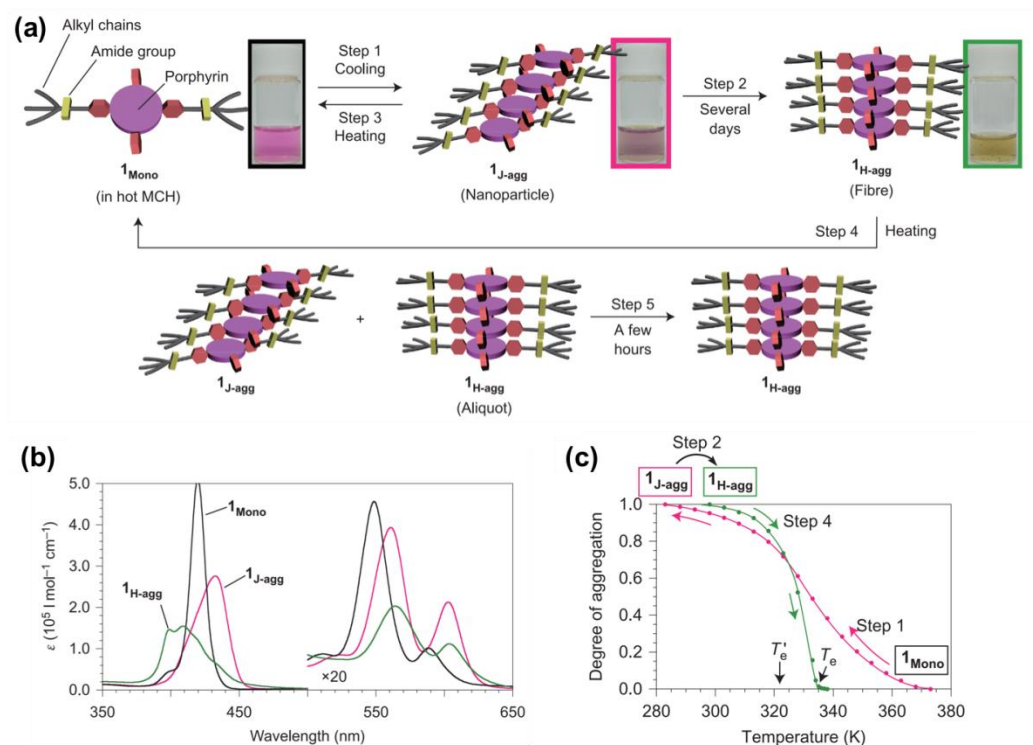
It should be pointed out that many other mild and highly efficient reactions may be utilized in supramolecular interfacial polymerizations. By marrying supramolecular polymer chemistry to conventional interfacial polymerization, supramolecular interfacial polymerization can be used to polymerize immiscible monomers in a controlled manner. It is highly anticipated that this facile strategy could be utilized in fabricating supramolecular materials with controllable properties, structures and functions.

### **3. Living Supramolecular Polymerization**

#### **3.1. Seeded Living Supramolecular Polymerization**

The “Holy Grail” of living supramolecular polymerization was reached by Sugiyasu, Takeuchi and co-workers based on seeded polymerization.<sup>[54]</sup> To achieve this goal, they elegantly designed a self-assembling system occurring out of equilibrium which is ubiquitously observed in nature. For example, amyloid fibril formation, observed in prion infection, has provided an important clue for supramolecular polymerization. A misfolded abnormal protein can aggregate to form amyloid fibril by converting the kinetically stable normal protein into the thermodynamically stable aggregates of abnormal proteins. To mimic such an “infection” process, they designed and prepared a porphyrin-based monomer as shown in **Figure 10**. By heating the solution of monomers to 368 K, all aggregates were disassembled to be monomeric state. When this solution was cooled from 368 K to 283 K (1 K min<sup>-1</sup>), nanoparticles were formed by J-aggregation. A typical redshift of the Soret band was induced with a sigmoidal transition, characteristic of an isodesmic assembly mechanism. This equilibrium should be described as a “pre-equilibrium”, because after several days the true equilibrium was reached through H-aggregation to form nanofibres. By heating the solution of nanofibres (1 K min<sup>-1</sup>), the absorption spectrum changed abruptly at the critical temperature ( $T_e$ ) with a non-sigmoidal transition, characteristic of a cooperative mechanism. The nucleation and elongation regimes were separated by the  $T_e$  temperature. These results

indicate that J-aggregation of nanoparticles is formed kinetically, but H-aggregation is favored thermodynamically.

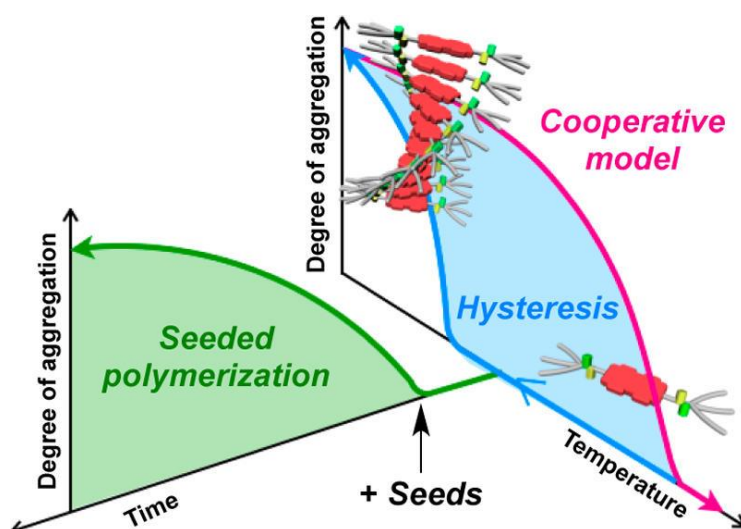


**Figure 10.** (a) Schematic representation of living supramolecular polymerization based on seeded polymerization; (b) UV-vis absorption spectra of monomer, its H-aggregation and J-aggregation; (c) Temperature-dependent degree of aggregation calculated from UV-vis absorption at 433 nm. Adapted with permission.<sup>[54]</sup> Copyright 2014, Nature Publishing Group.

Based on the understanding of the pathway complexity,<sup>[80]</sup> Sugiyasu, Takeuchi and co-workers elegantly devised a living supramolecular polymerization process. The monomer in this system is kinetically trapped and inert to spontaneous aggregation. Thus, the H-aggregated seed, with a relatively narrow polydispersity index (PDI) of 1.1 characterized by atomic force microscopy (AFM), was prepared by sonicating a solution of J-aggregates for 1 h. When this aliquot of seed nanofibres was added to a concentrated solution of J-aggregated nanoparticles, the solution rapidly became highly viscous without a lag time and finally

gelatinized. The logarithm of the apparent polymerization rate and the amount of the added seed were proportional to a slope of 1.01, indicating that the supramolecular polymerization is of first order with the characteristics of chain-growth polymerization. By adding solutions of J-aggregates into the obtained supramolecular polymers over four cycles, the PDIs were maintained at 1.1 for all stages, strongly indicating the living nature of the supramolecular polymerization.

Wuerthner and co-workers then further proved that this example of living supramolecular polymerization of a porphyrin molecule is not a special case.<sup>[81]</sup> By employing a widely studied perylene bisimide molecule, seeded living supramolecular polymerization was achieved and studied according to the thermodynamic and kinetic analysis as shown in **Figure 11**, which is identical for many other reported molecules. Essential for this seeded living supramolecular polymerization is to design a nucleation-elongation process coupled with a kinetically controlled pre-equilibrium.<sup>[82-83]</sup> In this way, spontaneous polymerization can be inhibited but living polymerization can be initiated by the addition of thermodynamically stable seeds.



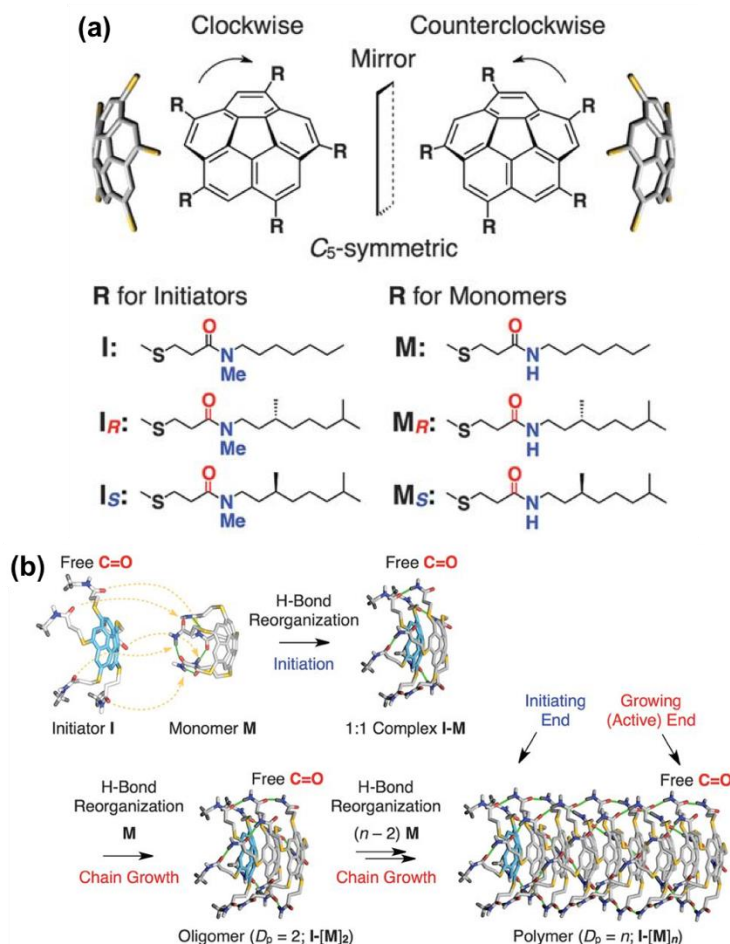
*Figure 11.* Schematic representation of the mechanism behind living supramolecular polymerization by employing a widely studied perylene bisimide molecule. Reproduced with permission.<sup>[81]</sup> Copyright 2015, American Chemical Society.

There is no doubt that this line of research represents a momentous step towards the progress and development of supramolecular polymer chemistry, and opens up a new avenue for living supramolecular polymerization. We highly anticipate that this research will inspire further investigations into controlling the nanostructures and functions of supramolecular organic materials by using various  $\pi$ -conjugated molecules.

### **3.2. Chain-growth Supramolecular Polymerization from Metastable Monomers**

In contrast with living polymerization in traditional polymer science, Aida, Miyajima and co-workers reported an inspiring piece of work for the realization of chain-growth supramolecular polymerization involving defined initiation and propagation steps.<sup>[55]</sup> To this end, they prepared a metastable monomer and a tailored initiator for their study. These species all contained a corannulene core with five amide-appended thioalkyl side chains as shown in **Figure 12a**. On account of their  $C_5$ -symmetric nonplanar bowl shape, such corannulene derivatives are chiral but racemization from bowl-to-bowl inversion can occur thermally even at 298 K. Previously, they reported that this monomer can assemble into a cage-like closed conformation in methylcyclohexane owing to the formation of an intramolecular hydrogen-bonding network through the amide units of the side chains.<sup>[84]</sup> Consequently, this specific corannulene-derived monomer cannot self-assemble spontaneously in methylcyclohexane. However, by heating the monomer in solution, it spontaneously polymerized into a one-dimensional assembly and continued to grow by addition further monomers. Upon obtaining these results, they designed an initiator that lacks the capacity to act as intramolecular hydrogen-bonding donor, but can serve as a proton acceptor for hydrogen bonding. This

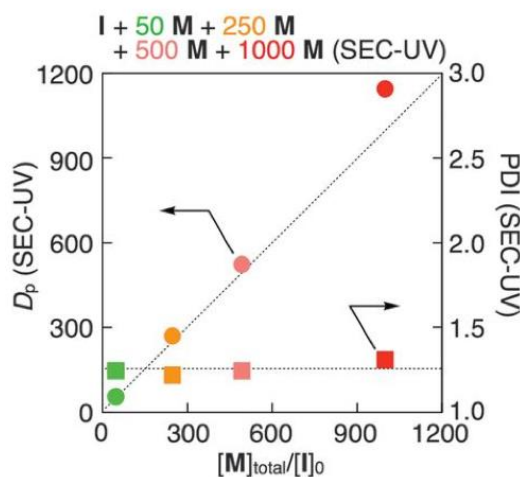
initiator, in a unidirectional fashion, can direct the intramolecular hydrogen-bonding network of monomers and initiate the chain-growth polymerization by shape-promoted  $\pi$ - $\pi$  stacking of the corannulene core to obtain the thermodynamically stable supramolecular polymers as shown in **Figure 12b**.



*Figure 12.*(a) Chemical structures of achiral and chiral monomers and initiators used by Aida and Miyajima and co-workers; and (b) the chain-growth supramolecular polymerization of monomer **M** initiated with **I**. Adapted with permission.<sup>[55]</sup> Copyright 2015, American Association for the Advancement of Science.

To implement the chain-growth supramolecular polymerization, a solution of the initiator was added to 50, 250, 500, 1000 equivalents of the monomer and the polymerization

performed at 298 K for 6 h. As shown in **Figure 13**, the polymerization degree of the supramolecular polymers, as confirmed by size-exclusion chromatography (SEC), increased perfectly with the ratio of monomer to initiator in a linear relationship over a wide range. Most importantly, the PDI values of the polymers obtained by SEC were all determined to be in a range of 1.2-1.3. Furthermore, they also explored the possibility of stereoselective polymerization by introducing the chiral side chains into the monomer and the initiator. Only the combination between the stereo-matched monomer and initiator would allow stereoselective helical chain-growth supramolecular polymerization. More interestingly, the chiral initiator can also serve as a chiral auxiliary to stereochemically induce polymerization to obtain homochiral supramolecular polymers by conformationally flexible monomers with achiral side chains. It should be noted that it is also possible to functionalize these supramolecular polymers by introducing functional side chains into the monomeric design.



*Figure 13.* Plots of the degrees of polymerization and PDI versus  $[M]_{\text{total}}/[I]_0$ , as estimated from the SEC-UV traces using polystyrene standards for calibration. Adapted with permission.<sup>[55]</sup> Copyright 2015, American Association for the Advancement of Science.

To successfully fabricate supramolecular polymers with a narrow PDI, the rational design of a metastable monomer is very crucial to this strategy. Without the concave structure

of monomer and intramolecular hydrogen-bonding network, the chain-growth supramolecular polymerization would not proceed. However, it is hoped that further structural diversification of metastable monomers may be realized to expand this strategy. This pioneering research establishes the foundation of chain-growth supramolecular polymerization from metastable monomers and opens up a new avenue for precise molecular engineering of supramolecular polymers.

#### **4. Conclusions and Outlook**

We have provided an overview of recently developed methods of supramolecular polymerization from controllable fabrication to living polymerization. The self-sorting approach and supramonomer method extend ways of thermodynamic control over supramolecular polymerization for controllable fabrication and supramolecular interfacial polymerization enriches the polymerization method of implementation. Moreover, seeded polymerization under pathway complexity and chain-growth polymerization from metastable monomers advance the kinetic controls over supramolecular polymerization with a living feature.

There is no doubt that fabrication of supramolecular polymers with controllable molecular weight and narrow distribution is a historical mission for scientists in the field of supramolecular polymers. Learned from covalent polymer science, more and more methods for controllable supramolecular polymerization could be explored, such as supramolecular emulsion polymerization, supramolecular suspension polymerization, ring-opening supramolecular polymerization and so forth. Devising new methods of living supramolecular polymerization under kinetic control is of great importance as well. In addition, supramolecular polymer physics needs to be explored. Various methods of controllable and living supramolecular polymerization would allow for fabrication of supramolecular polymers with controlled sequence and topological structure. Considering the dynamic nature of



supramolecular polymers, they can be reversible, stimuli-responsive, processable and self-healable materials, attributes that are not easily accessible by covalent polymers. It is highly desirable for combining molecular architectures with functional assembly, leading to advancement of molecular engineering of supramolecular polymers.

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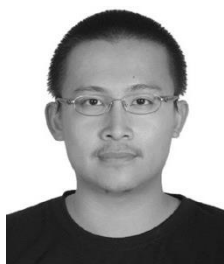
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#### Table of contents entry:

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### Supramolecular Polymerization from Controllable Fabrication to Living Polymerization

